

Salt hydration and drop drying of two model calcium salts: Implications for foliar nutrient absorption and deposition

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Abstract

Background: Hygroscopic salts are often applied as foliar fertilizers and calcium (Ca) salts have been used as model for cuticular permeability studies, with focus on their Point of Deliquescence (POD).

Aim: This study was aimed at characterizing water sorption and desorption processes at 20, 30, and 40°C temperature (T), of two model Ca salts commonly used as foliar sprays.

Methods: Trials were developed with pure Ca-chloride and Ca-nitrate salts in addition to 2 M and 150 mM Ca solutions. Salts were analyzed by Dynamic Vapour Sorption (DVS) and climate chamber experiments.

Results: For both Ca salts, water sorption and desorption processes followed hysteresis curves which varied with T. Salt POD was T-dependent and generally decreased with increasing T. For both Ca salts, the process of efflorescence began at or below 10% RH, at a certain level of water desorption Ca-salts becoming highly concentrated solutions (HCS).

Conclusions: Owing to the low point of efflorescence (POE) of both salts, drops of Ca-chloride and Ca-nitrate supplied as foliar sprays will not fully dry under normal RH and T conditions in most world areas. Both Ca salts have a similarly high foliar penetration potential despite their different POD. The significance of the results for the potential absorption of foliar fertilizers and salts by the foliage is discussed under an agronomic and eco-physiological viewpoint.

Key words: aerosols / agrochemicals / calcium / drops / fertilizers / foliar sprays / hygroscopic

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1 Introduction

Foliar fertilizer and agrochemical sprays of, for example, biostimulants are broadly used in agricultural production as tool for improving crop yield and quality (Fernández and Brown, 2013; Tanou et al., 2017). Many factors affect the process of foliar absorption which can be grossly grouped on those related to plants (e.g., plant physiology, anatomy, phenology or plant surface composition and structure), to environmental conditions at and after the time of treatment [e.g., effect of light, temperature (T), relative humidity (RH)], and finally to spraying technology and foliar formulation properties (e.g., active ingredient chemical form or addition of adjuvants (Fernández and Eichert, 2009; Fernández et al., 2013). A major chemical and structural heterogeneity has been described for the surface of different plant organs, species, varieties or developmental stages, which can ultimately lead to variable absorption rates at the time of foliar spray application (Fernández and Eichert, 2009). The effect of environmental conditions with emphasis on RH has been highlighted in several investigations as a key factor affecting foliar absorption (e.g., Schönherr, 2001; Burkhardt and Hunsche, 2013). Combined

RH and T effects can affect the mechanisms of absorption of foliar sprays both at the plant and the fertilizer formulation level (Fernández and Eichert, 2009). Some studies analyzed the performance of hygroscopic salts as aerosol particles in relation to foliar absorption (e.g., Schönherr, 2001; Schönherr and Luber, 2001) and stomatal penetration (Burkhardt et al., 2012), highlighting the importance of the point of deliquescence (POD) or deliquescence relative humidity (DRH) of the compounds.

Deliquescence is defined as a phase transformation of a crystalline solid to a solution that occurs above a critical RH value that corresponds to the POD which is specific for each substance or chemical mixture (Khvorostyanov and Curry, 2014; Allan and Mauer, 2016). Considering just a single, pure, solid chemical, if it is exposed to RH values from zero to below the POD, water molecules will adsorb to crystal surfaces in a semi-organized fashion or condense in tight spaces via capillary condensation, with limited dissolution (Thiel and Madey, 1987; Allan and Mauer, 2016). At the POD phase boundary, both the crystalline solid and saturated solution are thermo-

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dynamically stable (Mauer and Taylor, 2010), while water condensation and the formation of a saturated solution film at the crystal surface will occur at RHs above the POD (Allan and Mauer, 2016). As RH further increases, these patches merge and form a thin liquid film, which gradually thickens. Then, the entire solid particle dissolves and transforms into a solution drop, and its radius will abruptly grow (Khvorostyanov and Curry, 2014). After deliquescence, further hygroscopic growth is possible with increasing RH and in the case of many particles being together, drops will merge and solution of significant volume may be observed. When RH decreases after deliquescence, the reverse process of salt solution evaporation proceeds. However, solution drops do not transform back into solid particles at the same DRH (POD), but remain liquid down to substantially lower RH values (Khvorostyanov and Curry, 2014). Under such conditions, the solution becomes supersaturated with respect to solute concentration and is in a metastable state until reaching another threshold value, called efflorescence relative humidity (ERH) or Point of Efflorescence (POE). At or below this second RH threshold value, which is specific for each chemical compound or mixture, a phase transition into solid state or salt crystallization begins (Khvorostyanov and Curry, 2014). Hence, the processes of water sorption and deliquescence associated with hygroscopic growth at increasing RH are different from those related to subsequent water desorption, evaporation and efflorescence at decreasing RH. The deliquescence and efflorescence RHs of a compound depends on T and will generally increase with decreasing T (Khvorostyanov and Curry, 2014). This implies that at higher temperatures, lower RHs will induce deliquescence of hygroscopic inorganic or organic compounds and chemical blends, as thermodynamically modeled by, e.g., Lipasek et al. (2013). The water sorption and desorption dynamics experienced by a certain compound or chemical mixture for a whole range of RH variations are called humidity hysteresis (Khvorostyanov and Curry, 2014).

The effect of RH on hygroscopic compounds is actually a problem affecting the stability of for example, pharmaceutical products (Tereshchenko, 2015), food ingredients (Lipasek et al., 2013), wall paintings or buildings (Piqué et al., 1992). This is also a topic of major importance for meteorologists, because aerosol particle humidity hysteresis including POD and POE are involved in cloud physics in relation to, e.g., aerosol optical properties or cloud formation phenomena (Khvorostyanov and Curry, 2014).

Several studies evaluated the properties of inorganic hygroscopic particles chiefly in relation to the POD and using models and experimental procedures of variable complexity (e.g., Hu et al., 2010; Khvorostyanov and Curry, 2014; Ferrero et al., 2015; Allan and Mauer, 2016). Particle shape and size affect deliquescence and efflorescence of a hygroscopic salt, and are factors considered in several deliquescence prediction models (e.g., Russell and Ming, 2002; Khvorostyanov and Curry, 2014). In general, a decrease in particle size increases the surface: volume ratio of the crystals with an increase in equilibrium moisture content because of water sorption (Tereshchenko, 2015). For example, for NaCl particles of 100 nm diameter the POD is 75% and similar to its bulk value. However, when particle size decreases from 100

to 15 nm, a POD increase to 83% was estimated (Russell and Ming, 2002).

Calcium is an essential plant nutrient with many physiological and structural functions, including maintenance of cell wall integrity (Marschner and Rengel, 2012). The distribution of this element in plant organs is generally limited via the phloem and has been found to be associated with transpiration, leaves subsequently having increased Ca concentrations compared to low transpiring organs such as fruits (Montanaro et al., 2014; Song et al., 2018). Hence, the occurrence of physiological disorders related to localized Ca deficiencies in crop organs, such as fruits, has been reported for many species (White and Broadley, 2003). Recent findings point toward the role of the pedicel in supplying low amounts of Ca to the fruits once the xylem is sealed (Song et al., 2018). However, many studies developed with Ca fertilizers showed that the delivery of Ca to low transpiring organs is difficult to achieve unless Ca is supplied to their surface as foliar Ca sprays (Val et al., 2008; Koutinas et al., 2010). The processes of surface absorption and distribution of Ca in fruits are also complex and have variable efficacy (Val et al., 2008; Bonomelli and Ruiz, 2010) but optimizing fertilizer formulations and timing may be key for improving plant response to the treatments (Val and Fernández, 2011).

This study was motivated by a casual problem we faced when preparing a foliar Ca application experiment using a Ca-nitrate solution. Several hours (h) after application and expecting the drops to dry for being able to analyze the remaining salt deposits by scanning electron microscopy, we did not achieve this aim neither by heating the samples at 70°C in an oven nor by subjecting them to a 20% RH and 40°C for more than 1 h in a climate chamber. Then we recognized we were facing an unexpected challenge, and later on came into the account that this was likely associated with the POE of Ca-nitrate. After searching the literature, we grew aware that there are basically no data available on the POE of substances and also noticed that this parameter appeared to be difficult to evaluate theoretically.

Given the importance of Ca-chloride and Ca-nitrate as foliar fertilizers and aware of the existing POD values for such compounds (32% and 55% with no reference to T; Schönherr, 2001), we carried out specific trials for assessing their humidity hysteresis, POE, POD and process of drying of concentrated versus diluted solutions. Our hypothesis was that the POD is not the key factor affecting Ca solution drying as taken for granted in the existing foliar absorption literature.

2 Material and methods

2.1 Calcium compounds

Two different hygroscopic Ca salts were used (Sigma-Aldrich, Germany; Fig. 1A, E): anhydrous Ca-chloride (CaCl_2 , > 93%; granular form, with particle size ≤ 7.0 mm. Sigma-Aldrich code: C1016) and Ca-nitrate tetra-hydrate [> 99% purity; millimetric (< 1 to 5 mm long), thin crystals of variable shape, Sigma-Aldrich code: C1396]. Trials were performed with

pure salts (*i.e.*, with no additional anti-caking agents or chemicals), beginning either with solid salt particles, salt solutions or deliquesced (*i.e.*, after surpassing the POD and kept under high RH for several hours) initially solid salts (Fig 1).

2.2 Dynamic vapor sorption (DVS)

Dynamic vapor sorption (DVS) isotherms were performed on an Endeavour DVS, automated moisture sorption instrument (Surface Measurement Systems, Alpertown, UK) with between 8 to 33 mg of Ca salts. For the characterization of Ca salt performance under conditions commonly found in the field in many areas of the world, experiments were carried out at 20, 30, and 40°C. Prior to the beginning of DVS measurements, Ca salts were dried for 300 min under continuous air flow (0% RH) to establish the dry mass for each target T (20, 30, and 40°C, respectively). For analyzing water sorption, samples were subsequently exposed to increasing RH ranging from 0 to 95%, in 5% steps. When salts were approximately at their maximum water sorption capacity (stabilized at 95% RH), desorption curves were performed by lowering RH from 95 to 0%, also in 5% steps. The RH steps were maintained as long as relative mass variations with respect to time (dm dt^{-1}) remained below 0.01% for 10 min. The precision of DVS measurements was $\pm 0.5\%$ for vapor pressure and $\pm 0.1 \mu\text{g}$ for mass variations. From DVS sorption diagrams for a certain T, we estimated the POD as the maximum slope (first derivative) of the curve, excluding the steep change in mass observed at the high RH interval (80% and above). As for the POE, we analyzed the change in slope in the lower RH range of desorption diagrams obtained for a certain T and visually checked the state of HCS in climate chamber experiments, as described below.

Salt hydration state in the final phase of desorption experiments was estimated with following equation (Burnett and Thielmann, 2012):

$$W_{\text{molecules}} = \frac{MW_{\text{salt}} \times CM(\%) }{MW_{\text{water}} \times 100}, \quad (1)$$

where $W_{\text{molecules}}$ is the estimated hydration state, MW_{salt} is the molecular weight of the salt, MW_{water} is the molecular weight of water, and CM is the change in mass (%) for a given RH.

2.3 Climate chamber trials

For better interpreting DVS isotherm diagrams and establishing the potential RH to be associated with the POD and POE, complementary experiments were carried out under controlled T (20, 30, or 40°C) and RH (from 5 to 95%) conditions in a climatic chamber (MKF 56, Binder, Germany). Calcium salt water sorption and desorption processes at 20°C were analyzed gravimetrically with a precision balance (Mettler-Toledo, Spain). Pictures of the state of salts and/or salt solutions were taken at every step. Trials were also performed with 150 mM Ca solutions because this concentration is often applied as foliar sprays (*e.g.*, Val and Fernández, 2011). For estimating the desorption performance of concentrated solutions compared to deliquesced samples, experiments were also carried out with 2 M Ca-nitrate and Ca-chloride. In all trials, either 2 g of solid salt or 3 mL of solutions were deposited on to a Petri dish which had been previously weighed ($n = 4$). Samples were then kept in the climate chamber under controlled RH and T conditions and were assessed at regular time intervals. The physical state of salt particles and concentrated solutions was regularly evaluated with the naked eye and using an optical microscope (DM300, Leica Microsystems, Germany).

2.4 Data analysis

Statistical analyses were carried out with the programme SPSS 15.0 (SPSS Inc., USA). The remaining salt mass of different salts and of pure water over time were analyzed by one-way ANOVA. Tukey's Multiple Range Tests were performed to test differences between factors when F-values were significant ($p < 0.05$). Salt weight figures were plotted with Origin 9 software (USA).

3 Results

The dynamics of solid Ca-chloride and Ca-nitrate hydration/dehydration for a certain T and increasing or decreasing RH, followed several processes and ultimately led to state changes from solid to liquid or *vice versa*, as shown in Fig. 1, for experiments carried out at 20°C. For example, Fig. 1 (B, F) represents the theoretical POD for Ca-nitrate and Ca-chloride (60 and 30%, respectively), but an effect of particle size can also be clearly ascertained, since a high level of RH was required for Ca-chloride to become fully deliquescent, as shown in Fig. 1G. The process of salt crystallization also proved complex to identify and efflorescence began at 10% RH for Ca-chloride and below

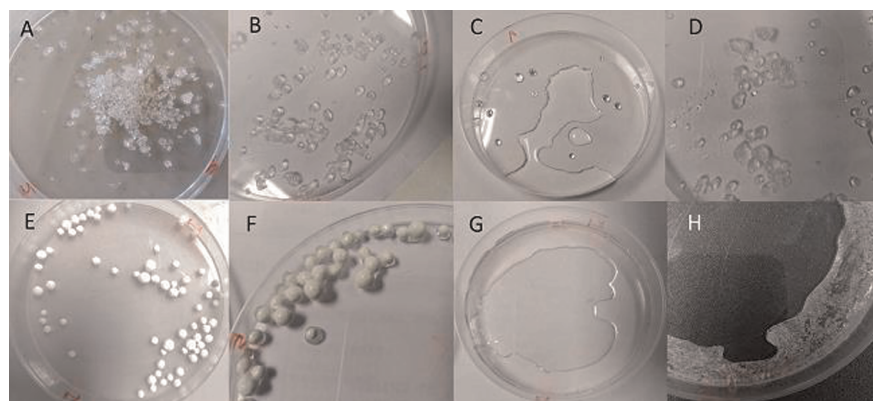


Figure 1: Images of 2 g of pure $\text{Ca}(\text{NO}_3)_2 \times 4 \text{H}_2\text{O}$ (A–D) and CaCl_2 (E–H) kept in a climate chamber, at 20°C and variable RH. (A, E) Dry Ca-salts at the beginning of the trial, (B) Ca-nitrate at POD (60% RH), (F) Ca-chloride at POD (30% RH), (C, G) hydrated salts (kept at 95% RH for 1 d), and (D, H) Ca salts after complete efflorescence (kept 1 d at RH < 10%).

this value for Ca-nitrate (Fig. 1D, H). Hence, for a fixed T (e.g., 20°C, as shown in Fig. 1) we recognized that it is difficult and even subjective to assign a concrete RH value for the POE and POD of a salt, and will subsequently refer to efflorescence (EP) or deliquesce (DP) phases once a threshold value is reached and a change of state is visible in certain areas of the highly concentrated Ca solutions (EP) or around solid particles (DP).

3.1 DVS isotherms

Experiments concerning water sorption and desorption processes at 20, 30, and 40°C are shown in Fig. 2 (Ca-chloride) and Fig. 3 (Ca-nitrate). From these DVS isotherm curves and visual observations on complementary climate chamber experiments, both the POD and POE were calculated for the three target temperatures (Tab. 1). The POD was estimated as the maximum slope point in sorption curves considering values up to a high RH (approximately > 80%), where another change in slope was noticeable (squares in Figs. 2 and 3). The POE is in the low RH interval (in general < 15%) of desorption isotherms (circles in Figs. 2 and 3), where a decrease in slope could be observed. Hence, while calculating POD was associated with the highest slope disregarding the high RH interval in sorption diagrams, identification the POEs was not possible from desorption isotherms and required the development of climate chamber experiments and visual observations (with an optical microscope and the naked eye). Interestingly, Ca salt POD values changed as a function of T. For CaCl_2 , the POD dropped 5% for each 10°C increase (Tab. 1). However, for Ca-nitrate, the POD significantly varied when T rose from 60% RH at 20°C to 20% RH at 40°C (Tab. 1). Remarkably, DP variation with T seems to be linear for Ca-chloride, but not for Ca-nitrate. For the EP, variation between salts and T used were not significant, always remaining in the range between 10 to 5% RH (Tab. 1).

Isotherms of both Ca-chloride and Ca-nitrate salts showed hysteresis between sorption and desorption curves in two different sections, i.e., high and low RHs (Figs. 2 and 3). At high RH, Ca-chloride isotherms showed the greatest hysteresis, i.e., up to 98% of change in mass at 20°C, while the maximum hysteresis of Ca-nitrate was 35% of change in mass at 20°C.

Hysteresis between sorption and desorption curves became negligible at 40°C, being the change in mass lower than 10% for Ca-chloride and 5% for Ca-nitrate.

At low RH, two different patterns were observed. For Ca-chloride solutions, the desorption experiment was finished with a higher weight compared to the initial one (i.e., the solid salt analyzed; Fig. 2). This implies that the final desorption phases corresponded to a hydrated Ca-chloride compound which was different from the initial one that was anhydrous. Interestingly, hydration states of final desorption phases were different for each experimental T. Such hydration state was estimated to correspond to 2, 3, and 4 water molecules at 20, 30, and 40°C, respectively. For Ca-nitrate, the final weight was lower than initial one and this was similar for the three T evaluated (Fig. 3). After such final desorption phase, Ca-nitrate was estimated to have 3 water molecules, i.e., one less compared to the initial solid salt used at the beginning of trials.

For the three T evaluated, we attempted to calculate the concentration of Ca-chloride and Ca-nitrate for the POD, POE and at maximum hydration (95% RH) but grew aware that in most cases we are dealing with HCS and performing calculations based on solutions may not be correct. Both salts are highly concentrated at the POD but become more concentrated when RH decreased to values close to the POE (data not shown).

3.2 Drying of diluted Ca solutions

For assessing the water loss process of Ca solutions commonly used as foliar sprays in agricultural production, the performance of 3 mL 150 mM Ca-chloride and 150 mM Ca-nitrate *versus* 3 mL of distilled water was estimated at 20°C and 15% RH as shown in Figs. 4 and 5.

Surprisingly, the rate of evaporation of Ca-chloride was faster than that of water and Ca-nitrate (Fig. 4), and this is cannot be directly related to the DP. However, from 560 min on, no significant differences in mass change over time were determined between samples. Once reached a certain threshold at 15% RH and 20°C, highly concentrated Ca solutions resem-

Table 1: Estimated POD and POE, and efflorescence phase for CaCl_2 and $\text{Ca}(\text{NO}_3)_2 \times 4 \text{H}_2\text{O}$, following a whole humidity hysteresis cycle (2 g solid salt per sample, $n = 3$).

Ca salt	T (°C)	POD ^a (% RH)	Efflorescence phase (% RH)	POE (% RH)
CaCl_2	20	30	10–5	10
	30	25	10–5	10
	40	20	8–5	< 10
$\text{Ca}(\text{NO}_3)_2 \times 4 \text{H}_2\text{O}$	20	60	8–5	< 10
	30	50	8–5	< 10
	40	20	8–5	< 10

^aHumidity was observed on the surface of salt particles below these RH values.

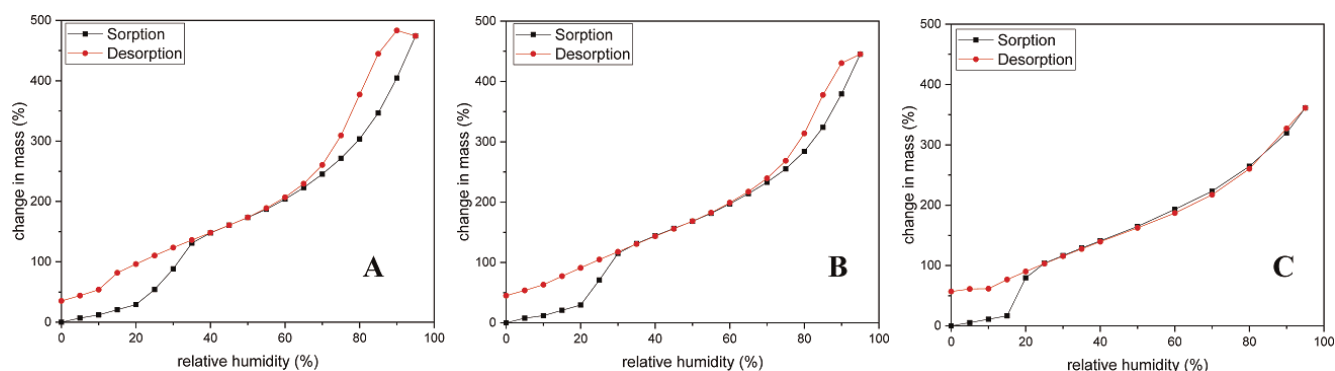


Figure 2: Dynamic vapor sorption isotherm curves of CaCl_2 at (A) 20°C, (B) 30°C, and (C) 40°C. Lines relate to sorption and desorption curves. The different DVS steps are represented with squares (sorption) or circles (desorption).

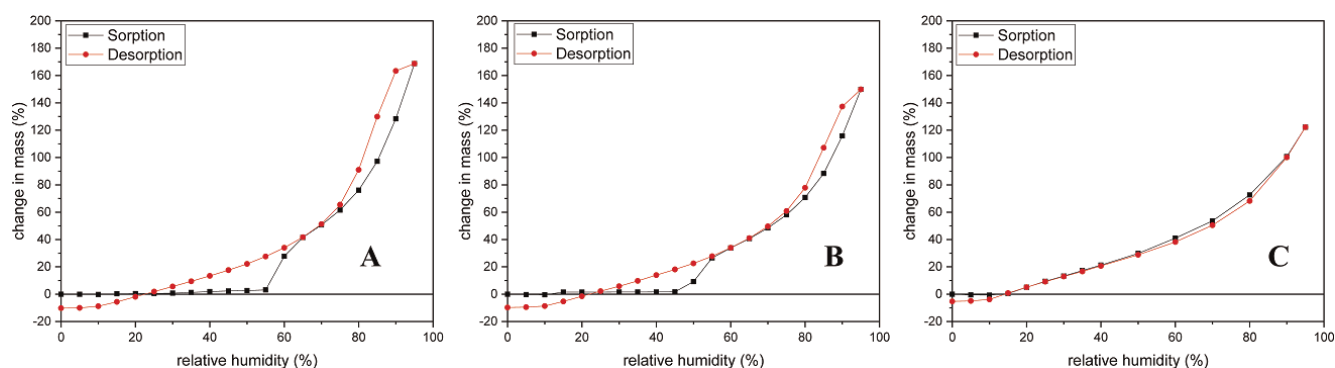


Figure 3: Dynamic vapor sorption isotherm curves of $\text{Ca}(\text{NO}_3)_2 \times 4 \text{H}_2\text{O}$ at (A) 20°C, (B) 30°C, and (C) 40°C. Lines relate to sorption and desorption curves. The different DVS steps are represented as squares (sorption) or circles (desorption).

bling those observed for pure salts (Fig. 1C, G) formed (Fig. 5C, D), with no measurable weight loss overtime. Such HCS were transparent and had an homogeneous appear-

ance, crystallizing only at $\text{RH} \leq 10\%$ for 20, 30, or 40°C, as observed with an optical microscope.

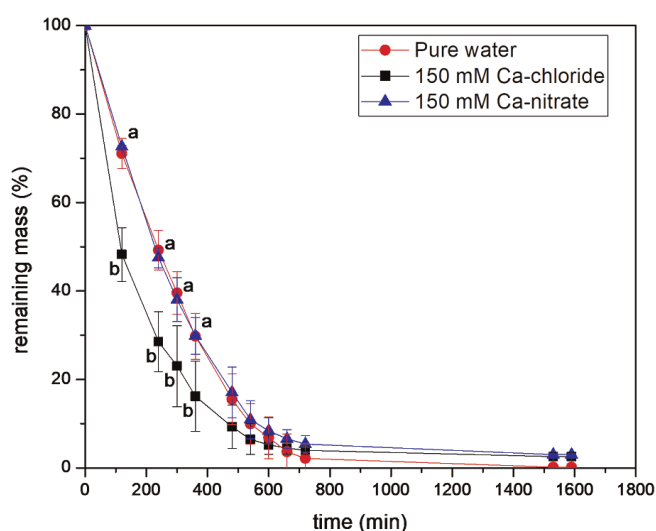


Figure 4: Remaining mass (%) of initial versus time (min) of 3 mL H_2O and 3 mL 150 mM Ca salts as $\text{Ca}(\text{NO}_3)_2 \times 4 \text{H}_2\text{O}$ or CaCl_2 , at 20°C and 15% RH ($n = 4$). Salts were still liquid at the end of the experiment. Bars represent the standard deviation (SD) of the mean. For each time and mean value, different letters indicate significant differences between Ca-nitrate and pure water (a) versus Ca-chloride (b).

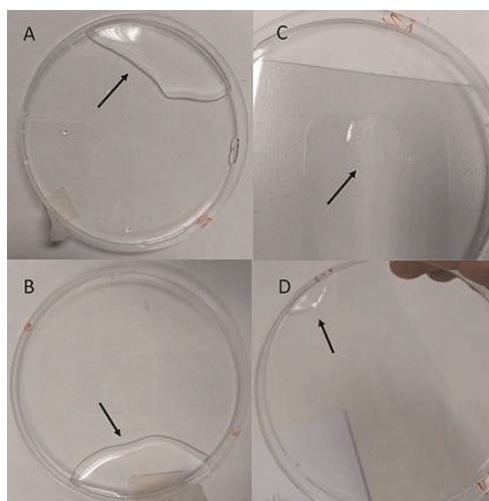


Figure 5: Images of 150 mM $\text{Ca}(\text{NO}_3)_2 \times 4 \text{H}_2\text{O}$ (A, C) and CaCl_2 (B, D) kept in a climate chamber, at 20°C and 15% RH for 2 d, corresponding to trials developed in Figs. 4 and 6. (A, B) 3 mL of 150 mM Ca salts applied at the beginning of the trial and (C, D) liquid sample remaining after 2 d at 20°C and 15% RH, where no weight loss was detected anymore (Fig 4). Highly concentrated Ca solutions in Petri dishes are indicated with an arrow.

3.3 Drying of concentrated Ca solutions and efflorescenced Ca salts

For evaluating if only highly concentrated Ca solutions have the capacity to retain water, trials were performed at 20°C and 15% RH for concentrated salt solutions and hydrated solid salts (kept at 95% RH for 1 d). As observed in Fig. 6, both concentrated salt solutions and hydrated solid salts had a similar performance for Ca-chloride and Ca-nitrate. In the case of both Ca compounds the weight loss after 600 min at 20°C and 15% RH was negligible and HCS were observed. These viscous Ca solutions formed after water desorption of either concentrated or diluted Ca-nitrate and Ca-chloride salt solutions and remained in an apparent equilibrium state, crystallizing only when setting the RH of the climate chamber at 10% or below.

4 Discussion

In this study, we characterized for the first time the humidity response at 20, 30, and 40°C of two Ca salts often used as foliar fertilizer sprays, *i.e.*, Ca-chloride and Ca-nitrate. Our aim was to develop trials that may help us understand the physico-chemical performance of drops of these two Ca salts when applied as foliar sprays. Our parting hypothesis that the POD is not the major factor affecting drying of hygroscopic Ca salt solutions was accepted, because efflorescence was found to be the prevailing physico-chemical phenomenon. Furthermore, deliquescence and POD of the Ca salts analyzed was much affected by T, while efflorescence was little affected by T changes. Water sorption and desorption isotherms showed different dynamics for variable T and RH regimes, indicating that the POD is not the most suitable parameter for predicting the process of drying of foliar fertilizer spray drops. Nonetheless, the POD of solid salt deposits will be important under increasing and changeable RH and T conditions (*e.g.*, at night or due to dew formation). However, diurnal RH and T changes in the field will lead to water sorption or desorption of concentrated salt solutions or salt deposits, following hysteresis processes in the case of hygroscopic

compounds. These dynamics may vary with the addition of, *e.g.*, anticaking agents (for increasing the POD) or humectants (for lowering the POD) to the foliar formulations and changing the properties of the mixture (Fernández and Eichert, 2009).

To our surprise, our DVS and climate chamber results showed that Ca-nitrate and Ca-chloride highly concentrated solutions failed to dry and crystallize until the very low RH threshold of 10% or below was reached, independently of T (at least for the 20 to 40°C range evaluated). Working with a model wettable surface (*i.e.*, a Petri dish), we recognized that the POE and the process of efflorescence of both salts will determine the rate of drying of a Ca-containing drops, the process being initially related to water evaporation in the case of diluted solutions (Fig. 4). We also observed that the water sorption and desorption dynamics followed different trends and varied within the T range evaluated which is representative for many areas of the world. Especially in the case of Ca-nitrate, we recorded a significant variation of the POD with T which dropped from 60% at 20°C to 20% at 40°C. Our results go against the assumption by Schönherr (2001) that the POD of Ca foliar fertilizers will not significantly vary with T. In the following paragraphs, the water sorption and desorption dynamics of Ca-chloride and Ca-nitrate will be discussed, considering also potential implications at least for plant nutrition and ecophysiology.

4.1 Ca salt water sorption and desorption

DVS measurements are commonly performed with drugs (Sheokand et al., 2014; Wu et al., 2012), wood (Patera et al., 2013; Simón et al., 2017) or construction materials (Bui et al., 2017; Jiang et al., 2019), for analyzing, *e.g.*, the stability, mechanical performance, hydration kinetics and amount of water that is adsorbed or desorbed by composite materials or chemical compounds (Suresh et al., 2017). For a certain T, this analytical method facilitates the detection of sample mass changes in response to RH variations, obtaining isotherms that may be useful for assessing, *e.g.*, the stability,

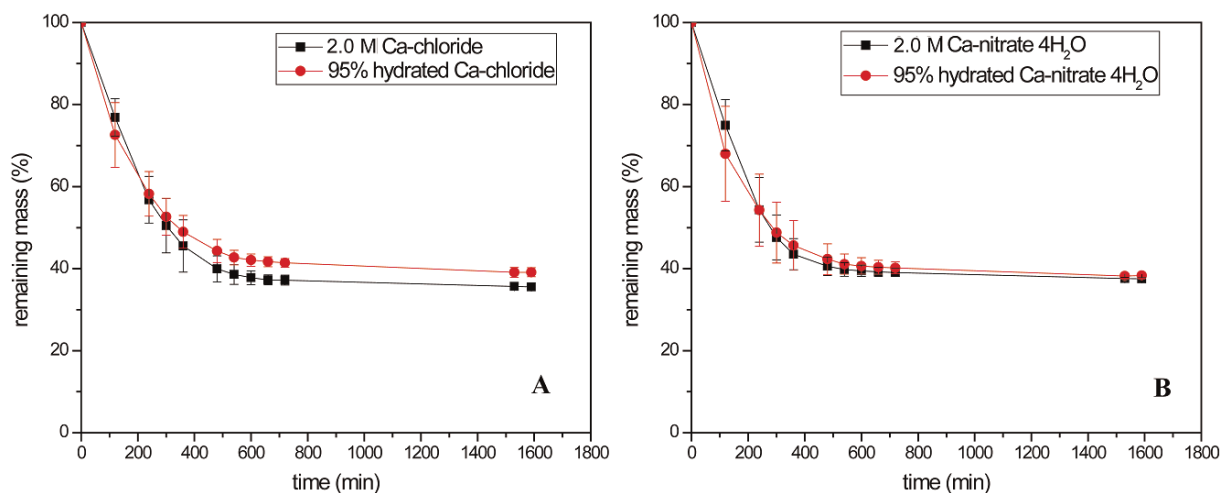


Figure 6: Remaining mass (% of initial versus current weight) of hydrated (1 d at 95% RH and 20°C) and 2.0 M CaCl_2 , versus (B) pure, hydrated (1 d at 95% RH and 20°C) and 2.0 M $\text{Ca}(\text{NO}_3)_2 \times 4 \text{H}_2\text{O}$. Salts were still liquid at the end of the trial. Data are means \pm SD ($n = 4$).

hydration state, polymorphism or adsorption/ desorption of water of different materials and chemicals (Simón et al., 2017; Suresh et al., 2017).

Analysis of Ca-nitrate and Ca-chloride by DVS enabled us to obtain isotherm curves for 20, 30, and 40°C, which did not follow the same pattern, once again indicating the T-dependence of salt hydration and dehydration processes. Both Ca salts showed hydration hysteresis as reported for other substances (Wu et al., 2012). However, in the case of Ca-nitrate a hysteresis reduction was observed for 40°C. This reduction of hysteresis with increasing T was reported by several authors for different materials (Hill et al., 2009; de Burgh and Foster, 2016; Simón et al., 2017; Almeida et al., 2018). Furthermore, the existence of this hysteresis implies that both Ca-chloride and Ca-nitrate liquids formed after the deliquescence are HCS. The occurrence of hysteresis in DVS isotherms is typical for hygroscopic materials and can be associated with mechanisms such as capillary condensation, fluid–fluid interactions or fluid–solid interactions (Patera et al., 2013). For example, hysteresis has been reported for highly porous or amorphous solids or stoichiometric hydrates (Sheokand et al., 2014) and also for transition changes or formation of stable or metastable species (Giron and Grant, 2008). The high concentration of the initially aqueous, but then saturated Ca salts upon dehydration, led to the formation of viscous concentrated Ca solutions which are likely to be metastable and impede the crystallization of Ca salts even after prolonged exposure to 15% RH, until RH was set at or below 10%. Few studies referred to this phenomenon (Wu et al., 2012) and further trials should characterize in detail the process of nucleation and crystallization of hygroscopic Ca and nutrient salts for the proper understanding of the mechanisms involved. The nature of the HCS formed after water evaporation should also be clarified, because it may be related to, e.g., a sol-gel formation or crystallization in aqueous solution processes, which are not described to date for highly hygroscopic salts. At low RH (e.g., 15%), we failed to see the formation of crusts or crystals in HCS by optical microscopy, until RH would be reduced to 10% or below. This suggests that Ca-chloride and Ca-nitrate crystallization from HCS may be kinetically hindered at high ion concentrations and might be for instance associated with a low nucleation rate in a highly viscous salt solution, as suggested by Balboni et al. (2011) for magnesium sulphate solutions.

It must be emphasized that 2 M Ca-nitrate and Ca-chloride subjected to 20°C and 15% RH performed as hydrated salt solutions and also formed HCS, alike 150 mM solutions after the initial evaporation phase (which took up approximately 700 min). Hence, the obtained patterns of water sorption and desorption of Ca-chloride and Ca-nitrate for 20, 30, and 40°C offer a complete picture of the hydration and dehydration performance of such salts and salt solutions/solid deposits. However, for interpreting the DP and suggested POD we must consider the preliminary characteristics of the salts including particle size and shape (Khvorostyanov and Curry, 2014), as also observed in climate chamber trials. Both Ca salt particles were in the mm range, but were larger and spherical for Ca-chloride and smaller and more angular for Ca-nitrate.

Calcium-salt hydration state changed during desorption. At the end of the desorption experiments carried out by DVS, efflorescenced Ca-chloride and Ca-nitrate salts had a different molecular weight from the initial one which may imply potential changes in, e.g., solubility or POD. Subsequently, further experiments should be carried out to quantify the hydration states of final phases and to determine if such phases are composed by only one phase or by different phases with diverse hydration states.

Another observation was that hydrated Ca-nitrate (*i.e.*, in the form of a viscous HCS) wetted the Petri dish in patches compared to the continuous film formed by Ca-chloride, suggesting a different surface tension of these Ca-containing compounds which may have implications for leaf wetting and foliar absorption. The physico-chemical nature of HCS of highly hygroscopic salts is currently unknown and should be characterized in future trials.

4.2 Agronomic and ecophysiological implications

Schönherr (2001) and Schönherr and Luber (2001) carried out trials to link the POD of Ca and K compounds to their rate of cuticular penetration and potential foliar fertilizer absorption. Focusing on the rate of penetration of 1 to 10 g L⁻¹ anhydrous Ca-salts supplied as chloride (32% POD), nitrate (55%), and three other organic forms (PODs from 95 to 10%) through isolated apple fruit or pear leaves cuticular membranes, various factors were analyzed including the effect of RH or adjuvants (Schönherr, 2001). Disregarding the role of T, the rates of cuticular penetration of Ca-nitrate and Ca-chloride at 100, 90, 80, 70, and 50% RH were determined. In spite of the higher POD of Ca-nitrate, Ca from this salt was transported at higher rates than Ca-chloride, with apparently no statistically significant differences between both Ca-salts (Schönherr, 2001). The author failed to justify this aspect and, however, interpreted an effect of the accompanying anion/s on cuticular transport which, up to now, is an unknown factor regarding foliar absorption mechanisms. However, these results can be justified based on our trials and the similar POE recorded for Ca-chloride and Ca-nitrate. Furthermore, the results obtained by Schönherr (2001) for Ca-nitrate and Ca-chloride cuticular penetration at decreasing RH suggest a negative effect of increased solution concentration at lower RH (e.g., 70%) compared to 90 or 100% RH, when drops will be more hydrated due to water sorption. An inverse relationship between increased solution concentration and relative foliar penetration rates has been described for several foliar or cuticular applied nutrients (Middleton and Sanderson, 1965; Bowen, 1969; Schlegel et al., 2006).

Future trials should characterize the performance of nutrient HCS after the evaporation of water in drops of foliar sprayed fertilizers and agrochemical mixtures, considering also the effect of humectants and anti-caking chemicals on the water sorption and desorption response of the mixture. A key question that arises is if after foliar treatment, the highly concentrated nutrient solutions formed in drops after water evaporation do enable foliar absorption of the applied nutrients, or if HCS are in equilibrium and do not favor the release of ions and subsequent foliar penetration process. In the field, drops

of foliar fertilizers deposited on to the foliage of crops or associated with leaf aerosol deposition in natural environments will be subjected to continuous T and RH changes, with diurnal water sorption and desorption cycles taking place in response to environmental conditions. Furthermore, the contribution of leaf wetness due to leaf transpiration (Burkhardt and Hunsche, 2013) to sorption and desorption processes of hygroscopic particles and/or highly concentrated nutrient solutions formed, e.g., after foliar fertilizer spraying, should be elucidated in the future using sensitive techniques and variable T and RH conditions (e.g., Burkhardt and Eiden, 1994; Burkhardt and Gerchau, 1994).

When searching for the lowest RH measured in different world zones, we learned that some areas of hyperdry Atacama Desert have mean atmospheric RHs of 17.3% (Azua-Bustos et al., 2015). Hence, the very low RH of 10% or below estimated for the initiation of the efflorescence phase for both Ca salts at 20 to 40°C made us become aware that drops of such foliar fertilizers will never dry in most areas of the world, despite this may not be visible with the naked eye after foliar spraying. Foliar absorption takes place on the liquid phase and liquid phase must exist between cuticle and solid salt residue for transport to occurs (Schönherr, 2001; Schönherr and Luber, 2001). Hence, once applied to the foliage, spray drops of diluted Ca-nitrate and Ca-chloride will evaporate until forming a HCS may be invisible and will be subjected to water sorption or desorption cycles as a function of at least, environmental RH and T changes. As already noted, the semi-liquid state of Ca in fertilizer drops deposited on to plant organs may favor or impede Ca foliar absorption, but this needs to be analyzed in future investigations.

Further implications can still be derived from our results, for instance, regarding leaf particle matter accumulation (Wang et al., 2013), the deposition of hygroscopic aerosols (Burkhardt, 2010) and their significance for foliar absorption processes (Burkhardt et al., 2012). Marine environments with high atmospheric salt concentration and humidity like in mangroves (Lovell et al., 2017) or sprinkler irrigation with saline water (Isa and Aragüés, 2010) will also lead to salt efflorescence and potential deliquescence cycles on to aerial plant surfaces. For example, the estimated POD and POE of sodium chloride are a 75% and 45% RH, respectively (Khvorostyanov and Curry, 2014). Hence, after saline water condensation or water drop deposition on the foliage (e.g., if sprinkler irrigated), liquid evaporation and processes similar to those described in this study will occur prior to salt efflorescence. Furthermore, salts in the liquid phase may be subsequently absorbed by aerial plant organs and induce physiological and metabolic responses (Isa and Aragüés, 2010). Thereby, consideration of the performance of salts in relation to ambient T, RH, and physical parameters like, e.g., particle size or shape, is a critical prerequisite for characterizing liquid–solid or solid–solid interactions between plant leaf/organ surfaces, and the absorption of foliar applied/deposited substances such as fertilizers or aerosols. Hence, deliquescence and efflorescence phenomena of mineral element solutions and/or particles deposited on to the foliage in response to RH and T among other factors, may ultimately induce phys-

iological effects in plants and should be taken into account in future investigations.

5 Conclusion

Our results show that an increase in T will lower the POD of the Ca-salts analyzed. However, no or just a slight variation was observed for the POE in relation to increasing T, values being extremely low for both Ca-salts (10% RH or below). Calcium-chloride and Ca-nitrate DVS isotherm diagrams showed hysteresis, a phenomenon which was also affected by T. During the first 6 h diluted Ca-chloride solutions loss water at a higher rate than Ca-nitrate when kept at 20°C and 15%. Then, highly concentrated Ca solutions formed and their rate of water loss was low and could not be detected gravimetrically. Concentrated 2 M Ca-containing solutions performed as 95% RH (1d, 20°C) hydrated solid salts regarding the rate of water desorption at 15% RH and 20°C.

It is concluded that rather than deliquescence, salt efflorescence and the rate of solution water desorption, are the most important factors affecting the process of drop drying of foliar fertilizers. Thereby, specific trials with various nutrient compounds and humectant should be carried out in the future for better characterizing the significance of these phenomena for foliar absorption-related affairs.

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